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(54) Title: A POLYVINYLIDENE FLUORIDE METAL-ADHESIVE COMPOSITION AND AN ELECTRODE FOR A BATTERY (57) Abstract <p>A polyvinylidene fluoride metal-adhesive composition where, in a composition composed of vinylidene fluoride homopolymer and vinylidene fluoride copolymer, one or both of these polymers has functional groups which show metal-adhesion, and the vinylidene fluoride copolymer content is from 0.5 to 50 wt.% of the total; and an electrode where, in an electrode for a battery in which the electrode compositional material layer comprising at least electrode active material and binding agent is formed on the surface of a current collector, there is employed as the binding agent the aforesaid polyvinylidene fluoride metal-adhesive composition.</p>		

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A polyvinylidene fluoride metal-adhesive composition and an electrode for a battery

The present invention relates to a polyvinylidene fluoride composition with outstanding metal-adhesion properties; a method for the production thereof; and an electrode for batteries which employs this composition as a binding agent.

Being melt-mouldable fluoropolymers of outstanding weatherability and chemical resistance, etc, poly-vinylidene fluoride and vinylidene fluoride copolymer resins are used in coating materials and for electrical/ electronic components, steel pipe linings, chemical plant components and weather-resistant/stain-resistant films, etc. However, since they have practically no adhesion to other materials, they suffer from the problem that they are difficult to modify or combine with other substances.

Hence, various attempts have been made to confer hydrophilic character, to enhance the adhesion properties and the dyeing/dispersion properties, etc, and to introduce crosslinking sites, etc, by the introduction of carboxylic acid groups into the polyvinylidene fluoride resin. For example, as a method for the introduction of carboxylic acid groups, there is known the direct introduction method by the copolymerization of vinylidene fluoride with a monomer having a carboxylic acid group, or a group convertible thereto, such as acrylic acid, methacrylic acid or the esters of these (Japanese Examined Patent Publication No. 2-604 and elsewhere).

However, in cases where the aforesaid procedure is adopted at the time of the production of a polyvinylidene fluoride resin containing carboxylic acid groups, there has been the problem that, on account of its copolymerization characteristics with fluorine-containing monomers, etc, the polymerization rate may be considerably lowered and only low molecular weight material obtained, unless there is used a special carboxyl-group-containing monomer requiring a

complex production process and, moreover, by introducing a copolymer component, the inherent properties of the polymer may no longer be obtained.

In Japanese Unexamined Patent Publication No. 50-41791, there is disclosed a method of grafting a fluoro-monomer which contains a carboxylic acid group, while irradiating with ionizing radiation, but, in addition to the industrial difficulties of employing radiation, this method also suffers from the problem of decomposition of the polymer main chains or accompanying crosslinking reactions occurring. Thus, in the case of the examples attempted hitherto in relation to fluorine-containing polymers, all have had associated difficulties when carried out industrially.

Now, turning to the lithium secondary batteries which have come to be employed in portable equipment such as mobile phones, video cameras and notebook-type computers, etc, in recent years, there can be used, as the negative electrode active material therein, a carbonaceous material such as coke or graphite which shows lithium ion doping and un-doping (Japanese Unexamined Patent Publication No. 62-90863), and as the positive electrode active material there can be used transition metal oxides such as manganese oxide and vanadium pentoxide, transition metal oxides such as iron oxides and titanium oxide, and composite compounds of these with lithium (e.g. lithium cobalt composite oxide, lithium cobalt nickel composite oxide and lithium manganese oxide), etc. In such circumstances, the electrodes are obtained by mixing a solvent with the mixture obtained by adding a suitable quantity of a binding agent to the powder-form electrode active material, to produce a paste, which is then coated onto a current collector, and dried, followed by press-bonding.

The binding agent employed in such secondary battery electrodes needs to have resistance to the organic solvent used in the electrolyte and resistance to the active species produced by the electrode reaction. Furthermore, solubility

in a specified solvent is required from the point of view of the electrode production process. Polyvinylidene fluoride (PVDF) resin is employed in most cases as a binding agent which satisfies these requirements. However, PVDF resin has inherently poor adhesion to metals and, in the case of both the negative and positive electrodes, the adhesive strength between the current collector and active material is inadequate following the press-bonding of the active material to the current collector, so there has been the problem that the active material tends to separate away from the current collector and the cycling characteristics of the battery become poor.

As a method for improving the bonding between the current collector and electrode active material, there has been proposed roughening the current collector surface (Japanese Unexamined Patent Publication No. 5-6766), but here too the adhesion still cannot be said to be adequate and a further improvement is required. Again, a copolymer of vinylidene fluoride and monomer containing a carboxylic acid group has been proposed (Japanese Unexamined Patent Publication No. 6-172452) but, normally, the copolymerization of a fluoro-monomer and another monomer having a carboxylic acid group is not easy, and raising production levels is difficult, so this approach cannot be said to be practical.

The present invention has the objective of offering a metal-adhesive polyvinylidene fluoride composition without impairing the solvent resistance, or mechanical or thermal properties, inherently possessed by a polyvinylidene fluoride resin and, moreover, where the metal-adhesion properties are conferred by a simple method; and a method for the production thereof; and also, by employing this composition as an electrode binding agent for batteries, of offering a battery electrode of enhanced adhesion between the electrode active material and the current collector.

The present inventors have discovered that if, in a mixture of vinylidene fluoride homopolymer and vinylidene

fluoride copolymer, at least one of these components has functional groups which exhibit metal-adhesion, then outstanding metal-adhesion properties are manifested. Furthermore, they have discovered that by using this composition as a binding agent for battery electrodes, the adhesion between the electrode active material and the current collector can be markedly improved. It is on these discoveries that the present invention is based.

Specifically, the present invention relates to a polyvinylidene fluoride metal-adhesive composition where, in a composition composed of vinylidene fluoride homopolymer and vinylidene fluoride copolymer, one or both of these polymers has functional groups which show metal-adhesion, and the vinylidene fluoride copolymer content is from 0.5 to 50 wt% of the total.

The vinylidene fluoride homopolymer employed in the present invention is obtained by the polymerization of vinylidene fluoride monomer by the suspension polymerization method or the emulsion polymerization method, etc, and preferably has a melt flow rate (MFR) at 230°C under a 2.16 kg load of from 0.005 to 300 g/10 min, and more preferably from 0.01 to 30 g/10 min.

Further, the vinylidene fluoride copolymer is a copolymer of vinylidene fluoride monomer and other monomer which can copolymerize therewith. The vinylidene fluoride component content in this copolymer will appropriately be from 50 to 95 wt%, and more preferably from 75 to 95 wt%. As the copolymerizable other monomer here, a fluoro-monomer such as tetrafluoroethylene, hexafluoropropylene, trifluoroethylene or trifluorochloroethylene is preferred, and one of these, or two or more, can be used. This resin can again be obtained by polymerization of the aforesaid monomers by the suspension polymerization or emulsion polymerization methods, etc, and preferably has a melt flow rate (MFR) at 230°C under a 2.16 kg load of from 0.005 to 300 g/10 min, and more preferably from 0.01 to 30 g/10 min.

In the present invention there are no particular restrictions on the functional groups which show adhesion (binding or affinity) in terms of metals, but as examples there can be cited carboxylic acid groups or carboxylic acid anhydride groups, carboxylic acid esters groups. Epoxy groups (glycidyl groups), mercapto groups, sulphide groups, oxazoline groups, phenolic groups are also effective.

In the present invention, the vinylidene fluoride copolymer contained in the composition composed of vinylidene fluoride homopolymer and vinylidene fluoride copolymer will be no more than 50 wt% of the total, preferably 0.5 to 20 wt% and, more preferably, from 1 to 10 wt%. If the vinylidene fluoride copolymer content is too low then there is an inadequate effect in improving the adhesion between metal materials and the PVDF composition, while if it is too great there is the effect that, due to a lowering of the chemical resistance of the PVDF composition, the adhesion to the metal material is impaired. In particular, where the PVDF composition is used as a binding agent for a battery electrode, swelling by the organic solvent used in the electrolyte (for examples, ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, etc) is increased and, in all cases, there are adverse effects on the properties of the electrode of the present invention or the secondary battery. In particular, such effects are considerable at temperatures above 50°C.

In the present invention, the methods for introducing functional groups which show metal-adhesion properties into both the vinylidene fluoride homopolymer and the vinylidene fluoride copolymer, or into one or the other, include (a) the method of effecting action, while heating, with an organic peroxide having a functional group which shows metal-adhesion, (b) the method of heat-treating in the presence of a peroxide and an unsaturated organic compound having a functional group which shows metal-adhesion. Other methods comprise : (c) the method of grafting an unsaturated or saturated organic compound having a functional group

which shows metal-adhesion, by using radiation, (d) the method of polymerizing vinylidene fluoride monomer, or this plus fluoro-monomer, using an unsaturated organic compound having a functional group which shows metal-adhesion as a copolymer component, (e) the method of polymerizing vinylidene fluoride monomer, or this plus fluoro-monomer using, as the initiator, an organic peroxide compound with a functional group which shows metal-adhesion, and (f) the method of using an unsaturated or saturated organic compound having a functional group which shows metal-adhesion as a chain transfer agent in the polymerization of vinylidene fluoride or this and fluoro-monomer.

In aforesaid method (a), carboxylic acid, carboxylic acid anhydride or carboxylic acid ester groups are readily introduced by subjecting the polyvinylidene fluoride resin to the action of an organic peroxide compound having at least one functional group selected from carboxylic acid, carboxylic acid anhydride and carboxylic acid ester groups, in the solution or molten state, while heating.

As examples of peroxide compounds having at least one functional group selected from carboxylic acid, carboxylic acid anhydride and carboxylic acid ester groups, there are disuccinic acid peroxide and di-t-butylperoxymaleic acid and the like. The reaction mechanism when the PVDF resin is heat-treated in the presence of such organic peroxides is not altogether clear, but carboxylic acid, carboxylic acid anhydride or carboxylic acid ester groups are introduced into the said resin.

In regard to reaction conditions in such circumstances, 100 parts by weight of the polyvinylidene fluoride resin is subjected to the action of from 0.5 to 100 parts by weight, and preferably from 1 to 20 parts by weight, of the organic peroxide having at least one functional group selected from carboxylic acid, carboxylic acid anhydride and carboxylic acid ester groups.

In aforesaid method (b), carboxylic acid or carboxylic acid anhydride groups are introduced by grafting, by the

heat-treatment of the polyvinylidene fluoride resin in the presence of a peroxide and an unsaturated organic compound having at least one functional group selected from carboxylic acid and carboxylic acid anhydride groups.

5 In such circumstances, as examples of the unsaturated organic compound with a carboxylic acid or carboxylic acid anhydride group used, there are unsaturated carboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, alkenylsuccinic acid,
10 acrylamidoglycolic acid and monoallyl 1,2-cyclohexanedicarboxylate, etc, unsaturated carboxylic acid anhydrides such as maleic anhydride and alkenyl-succinic anhydride, etc, and also derivatives of these.

Further, the peroxide used in method (b) is not
15 particularly restricted. Examples are peroxyketals, alkylhydroperoxides, dialkylperoxides, alkyl peroxy esters, diacylperoxides, peroxydicarbonates and peroxy-esters.

In methods (a) and (b), the heat-treatment of the PVDF resin in the presence of peroxide may be carried out in the
20 molten state or in a solvent, and can be employed in any such circumstances. Thus, when carried out in a solvent, the reaction can be performed, for example, with the PVDF resin and peroxide dissolved or dispersed in such solvent. Whatever reaction state is used, the heat-treatment should
25 be carried out under conditions such that the peroxide is adequately decomposed. Here, conditions such that the peroxide is adequately decomposed means a temperature of at least the 10-hour half-life temperature of the peroxide, for a reaction time in the range from 1 minute to 10 hours, and
30 preferably from 10 minutes to 5 hours.

The solvent used in methods (a) and (b) is not particularly restricted and is selected from water and organic solvents which are stable to peroxides. However, in order that the reaction be carried out uniformly and
35 efficiently, it is preferred that the reaction with the peroxide be carried out with the binding agent resin in the dissolved state. As examples of the PVDF resin solvents

employed here, there are N-methylpyrrolidone, N,N-dimethylformamide, dimethyl-acetamide, dimethyl-sulphoxide, tetramethylurea, acetone, methyl ethyl ketone and the like. Following the reaction, where required, the polymer is recovered as a precipitate, then washed with a solvent such as alcohol, and finally dried, to obtain the desired binding agent resin with carboxylic acid groups.

Functional groups introduced by the above methods remain in the resin at at least a certain fixed level, even following a purification process such as re-precipitation from solution or Soxhlet extraction by means of an organic solvent. Hence, they are regarded as being fixed to the PVDF resin by some form of chemical bonding. The amount of the carboxylic acid, carboxylic acid anhydride or carboxylic acid ester groups fixed (so that they are not removed by a purification process) to the polyvinylidene fluoride resin by the method of the invention in this way is from 0.002 to 2 meq and, more preferably, from 0.01 to 1 meq, per g of said dry composition.

The polyvinylidene fluoride metal-adhesive composition of the present invention can be employed as a binding agent in electrodes for a battery, where an electrode compositional material layer comprising at least electrode active material and binding agent is formed on the current collector surface. In this way, the adhesion between the electrode active material and the current collector is improved, and not only is it possible to prevent the electrode active material falling away from the current collector during the manufacture of the battery, but also there is ultimately obtained a battery electrode of improved cycling characteristics.

As the current collector in the electrode, there may be used a metal foil, metal mesh or three-dimensional porous body, etc, but it is preferred that the metal employed in the current collector be a metal which cannot readily alloy with lithium. In particular, iron, nickel, cobalt, copper,

aluminium, titanium, vanadium, chromium and manganese can be employed, on their own or as alloys thereof. ✓

Of the electrode active materials, the negative electrode active material should be a material which can
5 undergo doping and undoping with lithium ions. Examples of such materials are coke materials like petroleum-based or carbon-based coke, etc, acetylene black or other such carbon black, graphite, glassy carbon, active carbon, carbon fibre and carbonaceous materials such as fired organic polymers
10 obtained by the firing of organic high polymers in a non-oxidizing atmosphere. Moreover, copper oxide may also be added.

As the positive electrode active material, there are the aforementioned generally-used materials and there are no
15 particular restrictions. An electro-conductor may also be added thereto.

There may also be used as the binding agent a mixture of the aforesaid polymer with metal-adhesive functional groups such as carboxylic acid or carboxylic acid anhydride
20 groups and a polymer which does not have such functional groups. In such circumstances, the content of the former will preferably be at least 5 wt%, and more preferably at least 10 wt%, of the said binding agent.

As an example of the electrode production process, a
25 specified amount of the electrode active material and, as the binding agent, the polyvinylidene fluoride metal-adhesive composition of the present invention are kneaded in the presence of solvent. The slurry obtained is then coated onto the current collector, after which drying is performed,
30 followed by optional pressing, and the electrode obtained. In such circumstances, following the application of the slurry, a heat treatment is desirably carried out at 60 to 250°C, more preferably 80 to 200°C, for from 1 minute to 10 hours, according to the particular requirements. Strip-
35 shaped electrodes thus obtained may be wound into a roll shape (spiral shape) along with a strip-shaped separator and employed in the form of a wound electrode body.

As the solvent used for obtaining the slurry applied to the electrode current collector, there may be employed organic solvents such as N-methylpyrrolidone, N,N-dimethylformamide, tetrahydrofuran, dimethyl-acetamide, 5 dimethyl sulphoxide, hexamethylphosphoramide, tetramethylurea, acetone and methyl ethyl ketone, and water, either on their own or as mixtures thereof. Of these, N-methylpyrrolidone is especially desirably used. Further, where required, a dispersing agent may be added. In such 10 circumstances, a nonionic dispersing agent is preferably used.

The amount of the binding agent added to the electrode active material is preferably from 1 to 30 parts by weight, and more preferably from 3 to 15 parts by weight, per 100 15 parts by weight of the electrode active material. If the amount added is too great, or if it is too low, then it is not possible to obtain a high performance battery. Furthermore, where required, in the electrode compositional material layer, there may be added an electro-conductivity 20 conferring agent and/or other additives (copper oxide, etc).

In the case of the polyvinylidene fluoride metal-adhesive composition of the present invention, the swelling by the carbonate solvent normally used in a lithium battery is about the same as that of unmodified vinylidene fluoride 25 homopolymer. Further, in observations by DSC, a peak is observed in the vicinity of 170°C, which is the melting point of unmodified vinylidene fluoride homopolymer, so no deterioration in the heat resistance is apparent. Thus, the metal-adhesive composition of the present invention is 30 provided with all the properties required of a binding agent for the electrodes of non-aqueous lithium batteries and not just with adhesion to the current collector.

Below, the present invention is explained by means of examples, but the invention is not to be restricted in any 35 way by these examples.

Examples

Example 1

A solution formed by dissolving 100 parts by weight of polyvinylidene fluoride (made by Elf Atochem; Kynar 301F, MFR at 230°C under a 2.16 kg load = 0.03 g/10 min) and 2 parts by weight of disuccinic acid peroxide in 1000 parts by weight of N-methylpyrrolidone was heat-treated for 30 minutes at 120°C, after which the reaction liquid was poured into methanol and the polymer precipitated. This polymer was subjected to Soxhlet extraction for 24 hours with methanol under reflux, and the unreacted peroxide and peroxide decomposition products remaining in the polymer removed. From the magnitude of the absorption peak due to the carbonyl groups, in the vicinity of 1700-1800cm⁻¹, and that originating in the PVDF, at 881cm⁻¹, in the IR spectrum measured using film produced from this polymer, the carbonyl group content was found to be 0.085 meq/g, as calculated from a calibration curve separately constructed using mixtures of polyvinylidene fluoride and disuccinic acid peroxide.

A solution formed by dissolving 1 g of the polymer obtained and 0.1 part by weight of vinylidene fluoride/hexafluoropropylene copolymer (hexafluoropropylene content 10 wt%; made by Elf Atochem; Kynar 2801, MFR at 230°C under a 2.16 kg load = 0.2 g/10 min) in 10 g of N-methylpyrrolidone was coated onto copper sheet and aluminium sheet of thickness 1 mm and, after leaving for 1 hour at 120°C, drying was carried out under reduced-pressure.

When cuts at spacings of 1 mm were made in the surface of the polymer coating obtained and a cross-cut test (based on JIS K5400, 6.15) carried out, the percentage residual adhering PVDF coated layer was 100% for both the aluminium and copper sheets and, furthermore, when a tape peeling test was carried out, the residual percentage adhering was 95% in the case of the aluminium sheet and 100% on the copper sheet. Thus, it was confirmed that there was good adhesion

between the metal sheets and the polyvinylidene fluoride containing carboxylic acid groups. Further, when the polymer layer was peeled from the metal sheets and immersed for 72 hours at 60°C in ethylene carbonate, the degree of solvent swelling was found to be 27%. This was slightly raised when compared to unmodified Kynar 301F, but no great change was noted.

Example 2

10 A solution of 90 parts by weight of polyvinylidene fluoride (Kynar 301F), 10 parts by weight of Kynar 2801 and 2 parts by weight of disuccinic acid peroxide dissolved in 1000 parts by weight of N-methylpyrrolidone was heat-treated for 30 minutes at 120°C, after which the reaction liquid was
15 poured into methanol and the polymer precipitated. This polymer was subjected to 24 hours Soxhlet extraction under reflux with methanol, and polymer purification effected. The carbonyl group content calculated in the same way as in Example 1 from the IR spectrum, using film produced from
20 this polymer, was 0.15 meq/g.

A solution of 1 g of the resin composition thus obtained dissolved in 10 g of N-methylpyrrolidone was applied onto copper sheet and aluminium sheet of thickness 1 mm and, after leaving for 1 hour at 120°C, drying was
25 carried out under reduced pressure. When a cross-cut test was carried out as a test of the adhesion in the same way as in Example 1, the residual percentage adhering PVDF coated layer was 100% for both the aluminium and the copper sheet, and when a tape peeling test was carried out, the residual
30 percentage adhering was 90% for the aluminium sheet and 98% on the copper sheet. It was thereby confirmed that there was excellent adhesion between metal sheet and the polyvinylidene fluoride containing carboxylic acid groups. Further, the degree of swelling in ethylene carbonate
35 measured by the same method as in Example 1 using resin peeled from the metal sheet was 26%.

Example 3

A solution of 95 parts by weight of polyvinylidene fluoride (made by Elf Atochem; Kynar 301F), 5 parts by weight of Kynar 2801, 10 parts by weight of maleic anhydride and 10 parts by weight of lauroyl peroxide dissolved in N-methylpyrrolidone was heat-treated for 30 minutes at 100°C, after which the reaction liquid was poured into methanol and the polymer precipitated. This polymer was subjected to 24 hours Soxhlet extraction under reflux with methanol, and polymer purification effected. The carbonyl group content calculated in the same way as in Example 1 from the IR spectrum, using film produced from this polymer, was 0.055 meq/g.

A solution of 1 g of the resin composition thus obtained dissolved in 10 g of N-methylpyrrolidone was applied onto copper sheet and aluminium sheet of thickness 1 mm and, after leaving for 1 hour at 120°C, drying was carried out under reduced pressure. When a cross-cut test was carried out as an adhesion test in the same way as in Example 1, the residual percentage of adhering PVDF coated layer was 100% for both the aluminium and the copper sheet, and when a tape peeling test was carried out, the residual percentage adhering was 90% for the aluminium sheet and 95% on the copper sheet. It was thereby confirmed that there was excellent adhesion between metal sheet and the polyvinylidene fluoride containing carboxylic acid groups. Further, the degree of swelling in ethylene carbonate measured by the same method as in Example 1 using resin peeled from the metal sheet was 24%.

Example 4

A metal-adhesive resin composition was prepared in the same way as in Example 2, excepting that instead of the Kynar 301F in Example 2 there was employed a high-MFR polyvinylidene fluoride (made by Elf Atochem; Kynar 741, MFR at 230°C under a 2.16 kg load = 0.3 g/10 min). The carbonyl group content of the resin composition obtained was

0.04 meq/g, and outstanding metal adhesion was shown in the same way as in Example 2. Further, the degree of swelling by ethylene carbonate, measured by the same method as in Example 1 was 25%.

5

Example 5

Using, as a negative electrode active material support, coal pitch coke which had been subjected to grinding in a ball mill, 100 parts by weight thereof was mixed with 10 parts by weight of the polyvinylidene fluoride resin composition with carboxylic acid groups obtained in Example 2, as a binding agent, and then the mixture dispersed in N-methylpyrrolidone to form a slurry (paste). This slurry was applied to one face of aluminium foil of thickness 20 μm as the current collector, and dried for 20 minutes at 120°C to produce a negative electrode of thickness 110 μm and width 20 mm.

When adhesive tape was affixed to the electrode active layer on the surface of the electrode, and the adhesive strength between the current collector and the electrode active layer measured by means of a tensile testing machine, it was 220 g/cm. Further, after peeling, there was considerable adhering electrode active material remaining on the current collector, confirming that the adhesion between the electrode active material and the current collector was excellent. Moreover, in an adhesion test in which it was wound in the form of a roll onto an 1 mm cylinder, no separation of any electrode active layer was noted. Subsequently, when the electrode was immersed in ethylene carbonate and left for 3 days at 60°C, there was absolutely no separation of the electrode active layer.

Example 6

94 parts by weight of LiCoO_2 as the positive electrode active material, 6 parts by weight of graphite as an electro-conductive agent, and 10 parts by weight of the PVDF resin composition with carboxylic acid groups obtained in Example 3 as the binding agent, were mixed together, and

then the mixture dispersed in N-methylpyrrolidone to produce a slurry (paste). This slurry was applied to one face of copper foil of thickness 20 μm as the current collector, and dried at 120°C for 20 minutes, to produce a positive
5 electrode of thickness 110 μm and width 20 mm.

When adhesive tape was affixed to the electrode active layer on the surface of this electrode, and the adhesive strength between the current collector and the electrode active layer measured by means of a tensile testing machine,
10 it was 190 g/cm. Further, after peeling, there was considerable adhering electrode active material remaining on the current collector, confirming that the adhesion between the electrode active material and the current collector was excellent. Moreover, in an adhesion test in which it was
15 wound in the form of a roll around a 1 mm cylinder, no separation of any electrode active layer was noted. Subsequently, when the electrode was immersed in ethylene carbonate and left for 3 days at 60°C, there was absolutely no separation of the electrode active layer.

20

Comparative Example 1

A solution formed by dissolving 1 g of polyvinylidene fluoride (made by Elf Atochem; Kynar 301F) in 10 g of N-methylpyrrolidone was heated for 6 hours at 90°C, after
25 which it was cooled to room temperature, and applied onto copper sheet and aluminium sheet of thickness 1 mm and, after leaving for 1 hour at 120°C, drying was carried out under reduced pressure. When a cross-cut test was carried out in the same way as in Example 1 as an adhesion test of
30 the polymer-coated layer, the percentage residual adhering PVDF coated layer was no more than 20% for both the aluminium and the copper sheet. When a tape peeling test was carried out, all the PVDF peeled away. Further, the degree of swelling in ethylene carbonate measured by the
35 same method as in Example 1, using resin peeled from the metal sheet, was 23%.

Comparative Example 2

A solution formed by dissolving 1 g of the polyvinylidene fluoride resin with carboxylic acid groups obtained in Example 1 in 10 g of N-methylpyrrolidone, without the addition of Kynar 2801, was applied to copper sheet and aluminium sheet of thickness 1 mm and, after leaving for 1 hour at 120°C, drying under reduced pressure was carried out.

When a cross-cut test was carried out in the same way as in Example 1 as an adhesion test of the polymer coated layer, the residual percentage adhering PVDF coated layer was 100% for both the aluminium and copper sheets. When a tape peeling test was carried out, the residual percentage adhering was 50% for the aluminium sheet and at least 80% on the copper sheet. Thus, it was confirmed that the adhesion between the PVDF layer and the metal foil was inferior when compared to Example 1.

Comparative Example 3

As the negative electrode active material support, 100 parts by weight of coal pitch coke which had been subjected to grinding in a ball mill, and, as the binding agent, 10 parts by weight of polyvinylidene fluoride resin (made by Elf Atochem; Kynar 301F), were mixed together and then the mixture dispersed in N-methylpyrrolidone to produce a slurry (paste). This slurry was applied to one face of aluminium foil of thickness 20 μm , as the current collector, and then dried for 20 minutes at 120°C to produce a negative electrode of thickness 120 μm and width 20 mm.

When adhesive tape was affixed to the electrode active layer on the surface of this electrode, and the adhesive strength between the current collector and the electrode active layer measured by means of a tensile testing machine, it was found to be low, at 40 g/cm, and after peeling no residual adhering electrode active material was observed on the current collector. Furthermore, when the electrode was wound in the form of a roll around a cylinder of diameter

1 mm, about 20% of the electrode active layer separated away.

Comparative Example 4

5 As the negative electrode active material support, 100 parts by weight of coal pitch coke which had been subjected to grinding in a ball mill, and, as the binding agent, 10 parts by weight of the polyvinylidene fluoride resin with carboxylic acid groups obtained in Example 1, were mixed
10 together and then the mixture dispersed in N-methylpyrrolidone to produce a slurry (paste). This slurry was applied to one face of aluminium foil of thickness 20 μ m, as the current collector, and then dried for 20 minutes at 120°C to produce a negative electrode of thickness 120 μ m
15 and width 20 mm.

When adhesive tape was affixed to the electrode active layer on the surface of this electrode, and the adhesive strength between the current collector and the electrode active layer measured by means of a tensile testing machine,
20 it was slightly improved, at 80 g/cm, but after peeling no residual adhering electrode active material was observed on the current collector. Furthermore, when the electrode was wound in the form of a roll around a cylinder of diameter 1 mm, some separation occurred.

25

In accordance with the present invention, it is possible to obtain a metal-adhesive PVDF resin composition by a simple method, and without loss of the solvent resistance, or of the mechanical or thermal properties,
30 inherently possessed by polyvinylidene fluoride resin. When the metal-adhesive PVDF resin composition of the present invention is employed as a binding agent for battery electrodes, it is possible to produce electrodes with a high adhesive strength between the electrode active material and
35 the current collector. When such electrodes are employed in a secondary battery, not only is it possible to prevent separation between the electrode active material and the

current collector at the time of the battery production, but also there is obtained a secondary battery where there is no deterioration in the discharge capacity due to repeated charging and discharging.

Claims

1. A polyvinylidene fluoride metal-adhesive composition where, in a composition composed of vinylidene fluoride homopolymer and vinylidene fluoride copolymer, one or both
5 of these polymers has functional groups which show metal-adhesion, and the vinylidene fluoride copolymer content is from 0.5 to 50 wt% of the total.

2. A polyvinylidene fluoride metal-adhesive composition according to Claim 1 where the vinylidene fluoride copolymer
10 is a copolymer of vinylidene fluoride and at least one monomer selected from tetrafluoro-ethylene, hexafluoropropylene, trifluoroethylene and trifluorochloroethylene, and the proportion of the vinylidene fluoride component in this copolymer is from
15 50 wt% to 95wt%.

3. A polyvinylidene fluoride metal-adhesive composition according to Claim 1 and Claim 2 where functional groups which show metal-adhesion are introduced into both the vinylidene fluoride homopolymer and the vinylidene fluoride
20 copolymer, or into one or the other, by either (a) the method of effecting action, while heating, with an organic peroxide having a functional group which shows metal-adhesion, or (b) the method of heat-treating in the presence of a peroxide and an unsaturated organic compound having a
25 functional group which shows metal-adhesion.

4. A polyvinylidene fluoride metal-adhesive composition according to Claims 1 to 3 where the functional groups which show metal-adhesion are at least one functional group selected from carboxylic acid, carboxylic acid anhydride and
30 carboxylic acid ester groups.

5. A polyvinylidene fluoride metal-adhesive composition according to Claims 1 to 4 where the amount of the at least one functional group selected from carboxylic acid, carboxylic acid anhydride and carboxylic acid ester groups,
35 fixed to polyvinylidene fluoride resin, is from 0.002 to 2 milliequivalents per g of said dry composition.

6. A method for the production of a polyvinylidene fluoride metal-adhesive composition in which a mixture comprising vinylidene fluoride homopolymer and vinylidene fluoride copolymer, of vinylidene fluoride copolymer content 5 0.5 to 50 wt% of the total, is subjected to the action of an organic peroxide having at least one functional group selected from carboxyl, carboxylic acid anhydride and carboxylic acid ester groups, in the solution or molten state, while heating.

10 7. A method of producing a polyvinylidene fluoride metal-adhesive composition by the mixing of 0.5 to 100 parts by weight of vinylidene fluoride copolymer and 100 parts by weight of vinylidene fluoride homopolymer which has been modified by the action of an organic peroxide having at 15 least one functional group selected from carboxyl, carboxylic acid anhydride and carboxylic acid ester groups, in the solution or molten state, while heating.

20 8. A method of producing a polyvinylidene fluoride metal-adhesive composition according to Claim 6 or Claim 7 where the vinylidene fluoride copolymer is a copolymer of vinylidene fluoride and at least one monomer selected from tetrafluoroethylene, hexafluoropropylene, trifluoroethylene and trifluorochloroethylene, and the proportion of the vinylidene fluoride component in the copolymer is at least 25 50 wt%.

30 9. A method of producing a polyvinylidene fluoride metal-adhesive composition according to Claims 6 to 8 where 100 parts by weight of polyvinylidene fluoride resin is subjected to the action of from 0.5 to 100 parts by weight of an organic peroxide having at least one functional group selected from carboxylic acid, carboxylic acid anhydride and carboxylic acid ester groups.

35 10. An electrode which is characterized in that, in an electrode for a battery where the electrode compositional material layer comprising at least electrode active material and binding agent is formed on the current collector

surface, the binding agent being the polyvinylidene fluoride metal-adhesive composition according to Claim 1.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/02783

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09J127/16 C08L27/16 H01M4/62 //(C09J127/16,151:00),
(C08L27/16,51:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09J C08L H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 97 32347 A (ELF ATOCHEM S.A.) 4 September 1997 see claims; preparation example 3; example 4	1-5, 7-10
P, A	CHEMICAL ABSTRACTS, vol. 128, no. 25, 22 June 1998 Columbus, Ohio, US; abstract no. 308922, XP002078105 see abstract & JP 10 101726 A (ERUFU ATOKEMU KK) 21 April 1998 -/--	6



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/02783

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	CHEMICAL ABSTRACTS, vol. 127, no. 5, 4 August 1997 Columbus, Ohio, US; abstract no. 68544, XP002078106 see abstract & JP 09 129237 A (ERUFU ATOKEMU KK) 16 May 1997	1,6,10
A	EP 0 650 987 A (ASAHI GLASS CO., LTD.) 3 May 1995 see claims; examples 10,11	1,6

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Appl. No.

PCT/EP 98/02783

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9732347 A	04-09-1997	JP 9231977 A	05-09-1997
		AU 2023297 A	16-09-1997
EP 650987 A	03-05-1995	JP 7173446 A	11-07-1995
		US 5736610 A	07-04-1998
		JP 7173230 A	11-07-1995
		JP 7173447 A	11-07-1995